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ORIGINAL CONTRIBUTION

Alain Durand
Edith Dellacherie

Neutral amphiphilic polysaccharides: chemical structure and emulsifying properties

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A. Durand (✉) · E. Dellacherie
Laboratoire de Chimie Physique
Macromoléculaire,
UMR CNRS-INPL 7568,
Groupe ENSIC, BP 20451,
54001 Nancy Cedex, France
e-mail: alain.durand@ensic.inpl-nancy.fr
Tel.: +33-3831-75292
Fax: +33-3833-79977

Abstract Dextran, a neutral bacterial polysaccharide, is chemically modified by reaction with an aromatic epoxide (phenylglycidylether). The reaction conditions are either homogeneous, using dimethylsulfoxide as a common solvent, or heterogeneous, dispersing the epoxide into an aqueous solution of dextran. The grafting yield is much higher in homogeneous conditions. The viscometric characteristics of the amphiphilic polysaccharides are examined in water and in dimethylsulfoxide. These properties clearly depend on both the degree of substitution and the reaction conditions at a given degree of substitution. Highly modified dextrans (with more than 30% hydroxyl substituted) exhibit characteristic solubility in organic liquids that are non-solvents for the unmodified dextran. Changing the degree of hydrophobic substitution of the amphiphilic polysaccharide, direct and inverse submicronic emulsions are prepared. The stability of direct and inverse emulsions is analysed by following the evolution of the droplet size. Ostwald ripening is the major ageing process for both emulsions.

Keywords Polysaccharides · Polymeric surfactants · Emulsions

Introduction

Amongst amphiphilic copolymers, a large number are combinations of highly hydrophilic units with a low fraction of hydrophobic units. One way of preparing such copolymers is grafting hydrophobic hydrocarbon groups onto a hydrophilic polymer. This method has been largely applied since the initial paper of Landoll [1], which dealt with the preparation of hydrophobic cellulose derivatives by reacting the polymer with aliphatic epoxides. Nevertheless, a solvent able to solubilize the initial (hydrophilic) polymer as well as the hydrophobic reactant is generally difficult to find. According to how the various reactants are dispersed in the reaction medium, +IBw-homogeneous+IB0 or +IBw-heterogeneous+IB0 modification procedures have been developed. The term homogeneous generally refers to reactions carried out with both the polymer and the molecular reactants dissolved into the solvent used. On the contrary, heterogeneous reactions are carried out with one reactant in very poor solvent conditions or even phase-separated with only a low fraction dissolved. It has been demonstrated that, for a given polymer, changing the modification conditions from homogeneous to heterogeneous had significant effects on the polymer structure and properties. In particular, it has been shown that the distribution of hydrophobic substituents along the polymer backbone was in blocks in the case of heterogeneous reaction medium as compared to homogeneous conditions. In the case of amphiphilic derivatives of natural polysaccharides, similar work has been done with cellulose [2, 3]. In that case, four different sugar units can be encountered within the chains of methylcellulose [2]: unsubstituted, mono-, di- or trisubstituted sugar units. Using a convenient solvent, the authors were able to obtain a sample of methylcellulose with very different structural characteristics from the commercial ones that are obtained by a heterogeneous process in which cellulose remains undissolved.

The same problem is encountered for the preparation of amphiphilic polymers by copolymerization, and one efficient way has been introduced by Hill et al. [4] called four-micellar copolymerization. This copolymerization method allows the fine control of the microstructure of the copolymers and thus the rheological behaviour of their aqueous solutions [5].

In that work, we investigated the influence of reaction conditions on the preparation of amphiphilic derivatives of dextran, a neutral bacterial polysaccharide. The main objective was to determine reaction conditions allowing the preparation of dextran derivatives with hydrophobic modification varying in a wide range. The native polysaccharide was reacted with an aromatic epoxide, phenylglycidylether (PGE), under basic conditions. One procedure which involves a heterogeneous reaction medium has been introduced in our laboratory several years ago [6]. Here, that heterogeneous modification procedure was compared to a homogeneous one using dimethylsulfoxide (DMSO), a solvent common to dextran and PGE. The two modification procedures were compared. The modified polysaccharides obtained by the two methods were characterized through their solution behaviour in water and their emulsifying properties. The emulsion characteristics (type, droplet size and stability) are related to the amount of grafted hydrocarbon groups.

Materials and methods

Materials

The native dextran was obtained from Pharmacia (Uppsala, Sweden). This dextran sample, T40, has been characterized by size exclusion chromatography (SEC): $\overline{M}_n = 26,000 g/mol$, $\overline{M}_w = 40,000 g/moland$ $I_p = 1.6$. The other chemicals were from Aldrich (St. Quentin Fallavier, France) and were used as received. MilliQ water was used for all the experiments.

Polymer synthesis

Hydrophobic dextran derivatives were prepared by reacting dextran T40 with PGE following homogeneous and heterogeneous procedures.

In the homogeneous procedure, dextran (5g) is dissolved in an aqueous solution of tetrabutylammonium hydroxide (TBAOH) at room temperature. The molar ratio of TBAOH to sugar unit is 3:1. Then, the aqueous solution is freeze-dried. The resulting solid is dissolved in DMSO (200 mL) at room temperature. After several hours, the required amount of PGE is added dropwise to the solution. The reaction medium is left at room temperature for 4 days. After that time, the reaction mixture is dialysed against a water/ethanol mixture (50:50 v/v) and finally against water. The resulting aqueous solution is freeze-dried. In the heterogeneous procedure, dextran is dissolved in an aqueous solution of TBAOH (200 mL) at room temperature. The molar ratio of TBAOH to sugar unit is 3:1. After several hours, the required amount of PGE is added dropwise under vigorous stirring. The emulsified reaction medium is left at room temperature for 4 days. Then, the reaction mixture is dialysed against a water/ethanol mixture (50:50 v/v) and finally against water. The resulting aqueous solution is freeze-dried.

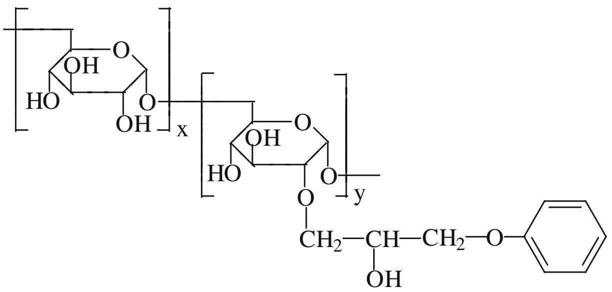
The degree of phenoxy substitution, τ (%), is defined by $\tau = 100\frac{y}{x+y}$ (see Scheme 1). The value of τ was determined by ^{1}H NMR in deuterated DMSO. The dextran derivatives used in that work possess degrees of substitution between 5 and 250%.

Size exclusion chromatography

The unmodified and modified dextran samples were characterized by SEC. The eluent was DMSO at 40°C. The flow rate was 0.7 mL/min and obtained by a Waters 590 pump. The column was of PLgel type, and the SEC detection system combined a differential refractometer Waters 410 and a light-scattering device miniDawn (Wyatt Tech. Corp.). With unmodified dextran samples, the average molecular weights obtained with that SEC system were identical to those obtained using water as the eluent. Since water was not convenient for modified dextran samples, DMSO was used.

Viscometry

Viscometric measurements with aqueous DexP solutions were carried out using an Ostwald-type capillary viscometer (0.46-mm diameter). The temperature was regulated by a circulating bath. Prior to measurements, the aqueous solutions were filtered through 0.2-μm filters. Polymer concentration was checked by weighting dry extracts obtained after leaving the solutions for 24 h in an oven at 110°C. The found values were always about 90% of the calculated ones. No kinetic corrections were required, because we verified that the flow time was proportional to the cinematic viscosity. In the case of water/DMSO mixtures, the time of solvent exhibited a pronounced maximum around 65% DMSO in volume, this is consistent with the results of Schichman and Amey [7].



Scheme 1 Note that this scheme does not imply that the same hydroxyl group is substituted within all the glucopyranose units. The detailed study of the position modified by vinyl glycidyl ether has not been performed

Interfacial tension measurement

Interfacial (dodecane/water) tension measurements were carried out at 25°C using a K8 surface tensiometer (Krüss, Germany) with a platinum ring. All samples were equilibrated for a sufficient time (15 min to 1 h) to reach constant readings.

Emulsion preparation

Oil-in-water emulsions were prepared by sonication (pulsed mode, 10 W, two sonication steps of 1 min separated by a rest of 2 min) using a Vibracell model 600W (Sonics & Materials Inc., Danbury, CT). Dodecane was used without further purification. The volumes of oil and aqueous phase were kept equal to 1 and 9 mL, respectively, for all emulsions prepared. The polymer was previously dissolved in the aqueous phase for 20 h.

Size measurement of emulsion droplets

Droplet and particle sizes were measured by dynamic light scattering at low concentration using an HPPS-ET from Malvern. Although this apparatus is able to measure relatively concentrated samples, the emulsions were diluted. For direct emulsions, dilution with oil-saturated water or with the polymer solution gave the same results. Consequently, pure water was used for diluting direct emulsions. In the case of inverse emulsions containing dichloromethane as the continuous phase, the dilution was performed in filtered dichloromethane after saturation with water. This saturation was necessary to avoid any droplet dissolution.

Dynamic light-scattering measurements with aqueous polymer solutions

The experiments were performed with the HPPS-ET from Malvern. The aqueous solutions were filtered through 0.2-μm filters before measurements. Polymer concentration was 10 g/L.

Results and discussions

Modification of dextran: comparison of homogeneous and heterogeneous procedures

In previous studies, dextran has been modified by PGE using a heterogeneous procedure [6]. The liquid PGE is dispersed under vigorous stirring into an alkaline aqueous solution of dextran (1 M NaOH). The emulsified PGE progressively reacts with the hydroxyl groups of dextran due to its (low) solubility in water. Provided that the reaction is continuous until completion, the droplets of epoxide completely disappear, and a clear aqueous solution is obtained (as long as the final modified dextran is fully water soluble). The sugar units are partly modified by formation of ether links (Scheme 1) by reaction between the hydroxyl groups and the epoxide. The degree of substitution, τ (%), is defined as the number of grafted PGE molecules within a series of 100 sugar units of the polysaccharide chain. Because three hydroxyl groups are present within one sugar unit, τ ranges between 0 and 300%.

Here, we use the same procedure as previously described [6] (see experimental), but for the sake of comparison, sodium hydroxide was replaced by TBAOH, because sodium hydroxide is not convenient for the second procedure (in DMSO). The series of polymers obtained following that procedure will be named DexP$_\tau$aq. To estimate the effect of the heterogeneity of the reaction medium, we applied another modification procedure where a solvent convenient for both dextran and PGE, DMSO, is used (see experimental). These conditions are called homogeneous, because dextran and PGE are fully soluble in DMSO. In the homogeneous procedure, TBAOH is also used as the base. The second series of polymers obtained will be named DexP$_\tau$org. At first sight, the great advantage of the heterogeneous procedure is that it involves a minimum of organic compounds, which makes it much easier and could be useful for large-scale developments. Similar considerations motivated studies about the synthesis of sucrose ethers or carbonates in aqueous heterogeneous medium [8–11].

The results of the two modification procedures were compared varying the amount of PGE initially added with a given amount of TBAOH (Table 1). It appears that, at a given amount of PGE, the degree of substitution obtained is much higher with the homogeneous procedure than with the heterogeneous one (Fig. 1). This can be explained by a partial hydrolysis of the epoxide when using the heterogeneous procedure [10]. In addition, increasing reaction temperature with the heterogeneous procedure significantly lowers the degree of modification of the recovered polymer (entries 9 to 11, Table 1). This may result from an increased hydrolysis of the epoxide because of its higher water solubility or from a difference in the activation energies of the two competitive reactions. With the homogeneous procedure, because water is reduced to a low amount in the reaction medium, the yield of modification is much higher. Around 70% of the added PGE is grafted onto dextran at the end of the reaction with the homogeneous procedure, while it is only 10% with the heterogeneous procedure (Fig. 1).

With the homogeneous procedure, varying the initial PGE to dextran sugar unit molar ratio up to 0.50, the resulting polymer remains fully soluble in water (up to 80 g/L). For ratios equal to 2 or 3, the polymer obtained is precipitated, and only a few percent is dissolved in water.

Table 1 Modification of dextran following homogeneous (1 to 6) or heterogeneous (7 to 11) procedures (for details, see text)

Reaction	Temperature (°C)	Polymer	[PGE]/ [Sugar unit]	τ (%)	Yield[a] (%)	$\overline{M}_n$[b] (g/mol)	$\overline{M}_w$[b] (g/mol)
–	–	T40	–	–	–	26,000	40,000
1[c]	RT	Dex	–	–	59	22,000	36,000
2	RT	DexP$_{17}$org	0.25	17	44	28,000	45,000
3	RT	DexP$_{33}$org	0.50	33	58	30,000	49,000
		DexP$_{54}$org	1.00	54	25	–	–
4[d]	RT	DexP$_{77}$org	1.00	77	51	25,000	39,000
5	RT	DexP$_{180}$org	2.00	180	73	45,000	75,000
6	RT	DexP$_{250}$org	3.00	250	66	62,000	100,000
7	RT	DexP$_{6}$aq	0.50	6	58	–	–
8	RT	DexP$_{23}$aq	2.00	23	36	–	–
9	RT	DexP$_{31}$aq	2.60	31	29	–	–
10	50	DexP$_{20}$aq	2.60	20	26	–	–
11	75	DexP$_{15}$aq	2.60	15	16	–	–

RT room temperature

[a] The yield is the ratio of the weight of recovered polymer to that of dextran and epoxide initially added

[b] The error on the molecular weight determination is ±1,000 g/mol

[c] This is a control reaction carried out following the whole procedure, except the addition of the epoxide

[d] For that reaction, the modified polymer was partly precipitated (DexP$_{77}$org) and partly dissolved (DexP$_{54}$org) in the final aqueous solution (see text)

For a ratio equal to 1, a significant part of the modified polymer (about 30 wt.%) is dissolved, but another fraction is precipitated in the final aqueous solution. The two corresponding samples are recovered separately and characterized (Table 1).

The polymers prepared by modification of dextran in DMSO were characterized by SEC in DMSO with 0.1 M $NaNO_3$ at 40°C. The number of average molecular weights obtained are generally 85% of the values calculated on the basis of the degree of substitution (Table 1). Moreover, these results show that dextran could be slightly degraded during that procedure (compare T40 and Dex in Table 1).

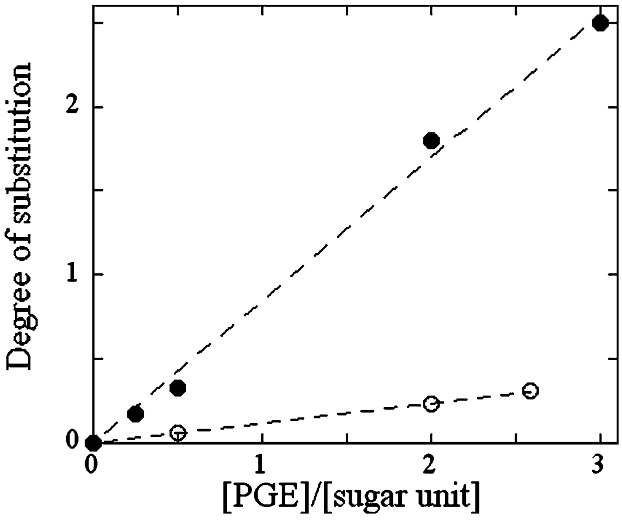


Fig. 1 Degree of substitution of dextran vs the molar ratio of epoxide to sugar units in the feed. ● Homogeneous procedure, ○ heterogeneous procedure

Characteristics of modified dextrans

The solution behaviour of the modified dextrans obtained by the two procedures was characterized by capillary viscometry in water (whenever possible) or in DMSO (for highly modified dextrans which exhibit very low water solubility) at 25°C (Table 2).

We first consider the DexP$_\tau$org series. The two polymers with the highest degrees of modification appear to be in good solvent in DMSO like unmodified dextran. The addition of small amounts of water leads to a significant decrease of the reduced viscosity (Fig. 2). For low amounts of water (less than 8% v/v), the decrease of reduced viscosity is comparable to that of unmodified dextran. It has been already demonstrated that DMSO is a better solvent for dextran than water [12–15]. The mutual affinity of DMSO and dextran has also been demonstrated by the plasticizing effect of this solvent in partially silylated dextran [16]. The plasticizing effect is significantly lower (about 15°C) than that predicted by the usual Fox relation [17]. This could be an indication of high affinity between solvent and polymer [18]. Moreover, the amount of residual DMSO in modified silylated dextrans was shown to be directly proportional to the number of unmodified hydroxyl groups [16]. For higher amounts of water, the effect seems to come mainly from the hydrocarbon groups. When the fraction of water exceeds

Table 2 Viscometric characteristics and hydrodynamic radii of dextran derivatives in water or DMSO at 25°C

Polymer	Solvent	$[\eta]$ (mL/g)	k_H	R_h (nm)[a]
T40	Water	20.0	0.5	5
	DMSO	28.4	0.5	–
Dex	Water	18.8	0.45	5
DexP$_{17}$org	Water	14.5	1.4	6
DexP$_{33}$org	Water	10.1	3.2	5
DexP$_{54}$org	Water	7.9	2.2	50
DexP$_{180}$org	DMSO	17.2	0.5	–
DexP$_{250}$org	DMSO	16.2	0.5	–
DexP$_{15}$aq	Water	14.0	1.0	–
DexP$_{31}$aq	Water	7.3	6.4	–

[a] Measured in water at 25°C at a polymer concentration of 10 g/L

30% v/v, the solution becomes cloudy and the polymer precipitates. For water-soluble dextran derivatives prepared in DMSO, we observe similar trends as evidenced for other dextran derivatives [19, 20]. The increase of τ leads to a lowering of the intrinsic viscosity, while the Huggins coefficient exceeds unity. For τ=54%, the polymer seems to be under the form of aggregates, which leads to low a k_H value as compared to other polymers with lower degrees of modification. This assumption was confirmed by dynamic light-scattering measurements in water (Table 2). This dextran derivative appears to be under the form of aggregates with a hydrodynamic radius around 50 nm, which is much higher than in the case of less-modified samples. As a result, for rather high degrees of modification, the macromolecules are mainly under the form of compact aggregates, and the fraction of isolated macromolecules, even in the dilute domain, remains probably low. A similar behaviour has been observed with hydrophobically modified pullulan samples, with much lower degree of modification (2%) but much more hydrophobic substituents (cholesteryl groups) [21]. Furthermore, for τ=54%, the aggregates seem to be so compact that the hydrocarbon groups become less available for intermolecular associations. This fact leads to a decrease of the Huggins coefficient. A similar effect has been observed with aliphatic hydrocarbon groups (n=10) but at much lower degrees of substitution (around 20%) [22].

When comparing the various dextran derivatives obtained by the two procedures, it appears that up to $\tau \approx 20\%$ the polymers have similar characteristics in water ($[\eta]$ and k_H). Nevertheless, for higher τ, the dextran derivative prepared by the heterogeneous procedure seems to have much less affinity for water: k_H is much higher than that of its homologue prepared in DMSO, and $[\eta]$ is significantly lower (Fig. 3). The decrease of intrinsic viscosity for dextran samples modified with the heterogeneous procedure is comparable to that observed when aliphatic hydrocarbon groups (C_n, n=6) are grafted using a homogeneous procedure [23] (Fig. 3). The results obtained by Nichifor and Carpov [20] for the modification of dextran by bile acid in the homogeneous medium are added for comparison. In that case, the decrease of the intrinsic viscosity is much sharper, which comes from the hydrophobicity of the grafted groups. According to the authors, the bile acid-modified dextrans are not water soluble for degrees of modification exceeding 6%. At 6% modification, the intrinsic viscosity is about 40% that of the native dextran. The same value is reached at 31% with phenoxy groups grafted with the heterogeneous procedure, while much higher values of τ are necessary with the homogeneous

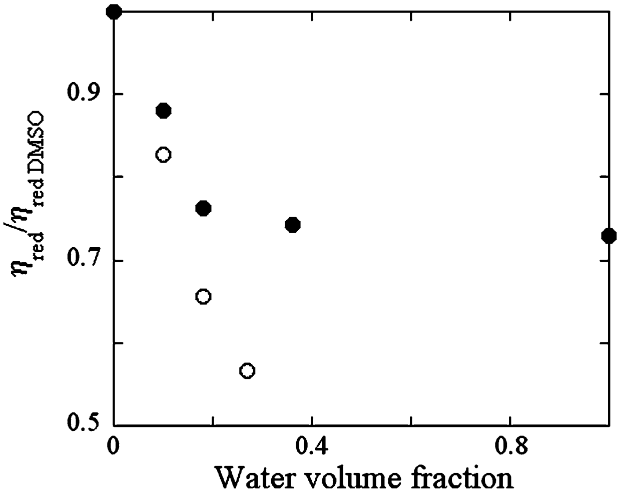


Fig. 2 Ratio of the reduced viscosity of polymer solutions in the water/DMSO mixture to that of the polymer solution in DMSO. ● Native dextran, ○ DexP$_{180}$org. The concentration of the polymer is 20 g/L. T=25°C

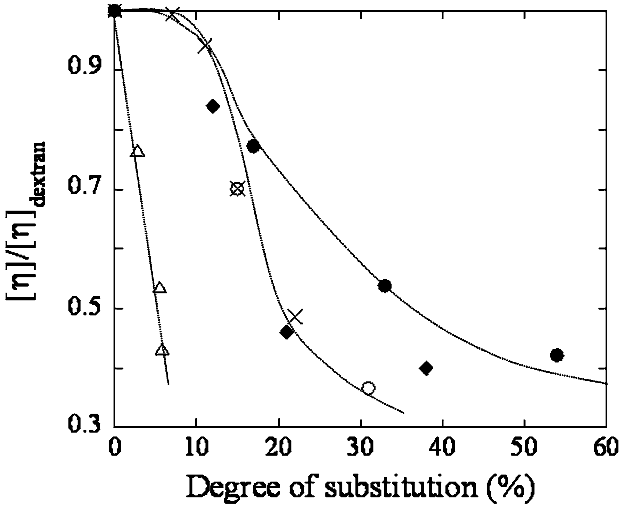


Fig. 3 Ratio of the intrinsic viscosity of modified dextrans to that of the native dextran vs the degree of substitution, in water at 25°C. ● DexP$_{\tau}$org, ○ DexP$_{\tau}$aq (this study), × DexP$_{\tau}$aq [19], ♦ dextran modified by aliphatic hydrocarbon groups with six carbon atoms [23], Δ dextran modified with bile acid [20]. *Lines* are guides for the eyes

procedure. The hydrophobic effect of phenoxy groups seems to be enhanced by the heterogeneous grafting procedure.

Previous studies about cellulose [2] lead us to assume that this difference comes from the microstructure of the modified dextrans and particularly from the distribution of the modified hydroxyl groups within the sugar units. Moreover, in the synthesis of sucrose carbonates, polysubstitution was shown to be favoured in aqueous medium [8]. Nevertheless, the detailed study of that point has not been performed yet to confirm that assumption.

The results obtained via the heterogeneous procedure are consistent with a previous study in which sodium hydroxide was used as the base instead of TBAOH [19] (Fig. 3). No significant effect of the base can be evidenced here.

Solubility of highly modified dextrans in organic solvents

The solubility of modified dextrans in organic solvents is strongly dependent on the degree of modification and on the type of groups attached [24]. Nevertheless, the available data are centred on the solubility in water and generally do not consider organic solvents. Some graft copolymers obtained by controlled chain polymerization initiated from dextran sugar units exhibit solubility in organic solvents, depending on the number and length of the grafts [25, 26].

We examined the solubility of modified dextran derivatives in several organic solvents (Table 3). The behaviour of the two highly modified polymers differs strongly from that of the initial dextran. They can be dissolved into solvents that are not miscible with water, provided that these are previously saturated with water. Such result was obtained with dichloromethane, chloroform, benzyl benzoate and ethyl acetate. This fact can be explained by taking into account the following considerations. In previous work, dextran has often been modified by ester groups [24, 27–30]. In that case, for each substituent attached onto a sugar unit, one hydroxyl group is lost. In the case of the modified dextrans prepared in our work, because one hydroxyl group is formed by opening the epoxide, the number of hydroxyl groups in a chain remains constant whatever the degree of substitution (Scheme 1) is. As a result, the organic solvents that can solubilize hydrocarbon moieties need the presence of traces of water.

Table 3 Solubility of DexP$_{180}$org in several organic solvents

Solvent	Solubility test[a]
Water	−−
Ethanol	−−
Acetone	−−
Tetrahydrofuran	++
Dioxane	++
Phenoxy-2-ethanol	++
Chloroform saturated with water[b]	++
Dichloromethane saturated with water[b]	++
Ethyl acetate saturated with water[b]	++
Benzyl benzoate saturated with water[b]	++

A fixed amount of polymer (0.025 g) is mixed with 5 mL of solvent for 24 h at room temperature. The visual result is indicated

[a] ++, clear solution; −−, undissolved solid with clear solvent

[b] With dry solvent, the result is “undissolved solid with clear solvent”

Emulsifying properties of amphiphilic dextrans

Hydrophobically modified dextrans are efficient polymeric surfactants as demonstrated previously in the case of water-soluble derivatives [19, 20, 28, 31–33]. The surface-active properties of non-water-soluble graft copolymers based on dextran have been demonstrated recently [26]. Nevertheless, no data are available about water-in-oil emulsions stabilized by dextran derivatives.

According to the rule proposed long ago by Bancroft [34], dextran derivatives soluble in organic solvents should be able to stabilize water-in-oil emulsions. With molecular surfactants, the hydrophilic–lipophilic balance (HLB) concept is a usual concept to rationalise the notion of “hydrophobic surfactant” and “hydrophilic surfactant”. In the case of polymeric surfactants like those considered in that work, the concept of HLB is difficult to employ even if some attempts have appeared [35, 36].

We studied the type of emulsion formed (direct or inverse) as a function of the oil volume fraction and the nature of the oil (Tables 4 and 5). The type of emulsion was determined by a dilution test immediately after preparation. From these results, it is clear that non-polar oils (dodecane or silicon oil) cannot give inverse emulsions in the presence of modified dextran even at high volume fractions. On the contrary, more polar oils (like esters or chlorinated alkanes) give inverse emulsions for oil volume fractions higher than 0.50. This fact is illustrated with benzyl benzoate but has

Table 4 Type of emulsion obtained with an aqueous solution of DexP$_{54}$org (5 g/L) and various oils

Oil	Emulsion
Octamethyltrisiloxane	O/W[a]
Dodecane	O/W[a]
Dodecane/Dichloromethane (75/25, v/v)	O/W[a]
Dodecane/Dichloromethane (50/50, v/v)	W/O
Dodecane/Dichloromethane (25/75, v/v)	W/O
Dichloromethane	W/O
Benzyl benzoate	W/O
Ethyl acetate	W/O
Olive oil	W/O

The volume fraction of oil is 0.91

[a] The O/W emulsion is obtained with a large excess of oil

Table 5 Type of emulsion obtained with water and two different oils

Polymer	Oil	ϕ				
		0.10	0.25	0.50	0.75	0.90
DexP$_{54}$org	Dodecane	O/W	O/W	O/W[a]	O/W[a]	O/W[a]
DexP$_{54}$org	Benzyl benzoate	O/W	O/W	O/W	W/O	W/O
DexP$_{250}$org	Benzyl benzoate	O/W	O/W	O/W	W/O	W/O

The polymer is either dissolved initially in water (DexP$_{54}$org) or in the oil (DexP$_{250}$org) at a concentration of 5 g/L. Different initial oil volume fractions (ϕ) are used

[a] The O/W emulsion is obtained with a large excess of oil

been also observed with other polar oils like dichloromethane (data not shown). Whether the polymer is initially dissolved in oil or in water does not change the result (Table 5). At a given oil volume fraction, varying the composition of the oil results in a change in the type of emulsion as illustrated with mixtures of dodecane and dichloromethane (Table 4). Finally, the oil volume fraction and the oil nature (more precisely its polarity) appear to be the more relevant parameters for the type of emulsion obtained. We can notice that inverse emulsions can be obtained with the amphiphilic polymer dissolved either in the aqueous phase or in the oil phase provided with convenient oil volume fraction and oil polarity. The strong effect of oil polarity is related to the high hydrophilicity of the polysaccharide backbone. A similar effect has been reported in the case of *N*-alkyl glucoside surfactants [37].

For oil-in-water emulsions, it has been demonstrated that the initial droplet size is mainly controlled by the polymer-to-oil weight ratio [38]. For low values, the droplet size depends on the relative amount of polymer available for covering droplet surface, and at high values, the droplet size is limited by the conditions of emulsification. When comparing the initial droplet size obtained with dextran samples modified by either the homogeneous or the heterogeneous one, we see that there is a significant difference (Table 6). The polymeric surfactants prepared by the heterogeneous procedure seem to produce much lower initial droplet sizes. The origin of this difference is still not clear, and further investigations are ongoing.

As for the ageing process of oil-in-water emulsions, it has been demonstrated in previous publications that it was mainly driven by Ostwald ripening [32, 33]. This ageing process results from the thermodynamic tendency of the oil to diffuse from small droplets to bigger droplets. When this process is predominant, the cube of average droplet radius increases linearly with time. A theoretical expression has been established independently by several authors [39, 40] to depict that variation of the average droplet radius:

$$\overline{R}^3(t) = \overline{R}^3(0) + \omega t \tag{1}$$

$$\text{with } \omega = \frac{8\gamma_i D V_m^2 C_\infty}{9RT} \tag{2}$$

In Eq. (1), $\overline{R}$ is the average radius of the droplets (m), t is the time (s) evolved since emulsion preparation and ω (m^3/s) will be named the “rate of Ostwald ripening” even if its units are volume per time.

In Eq. (2), γ_i is the interfacial tension (N/m), D is the diffusion coefficient of the oil in water (m^2/s), V_m is the molar volume of the oil (m^3/mol), C_∞ is the solubility of the oil in pure water (mol/m^3), R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K). The initial derivation was for infinite dilution, and consequently, the volume fraction of disperse phase (ϕ) does not appear in the

Table 6 Ostwald ripening rates of dodecane-in-water emulsions stabilized with water-soluble amphiphilic dextrans

Polymer	γ_i (mN/m)[a]	Initial droplet size (nm)[b]	ω_{exp} (m^3/s)	ω_{calc} (m^3/s)	$\omega_{exp}/\omega_{calc}$
DexP$_{17}$org	11	313	2.56×10^{-26}	4.53×10^{-27}	5.7
DexP$_{33}$org	7	266	1.74×10^{-26}	2.94×10^{-27}	5.9
DexP$_{54}$org	7	428	1.74×10^{-26}	2.79×10^{-27}	6.3
DexP$_{6}$aq	24	225	3.11×10^{-26}	10.3×10^{-27}	3.0
DexP$_{16}$aq	15	193	2.53×10^{-26}	6.47×10^{-27}	3.9
DexP$_{31}$aq	9	214	1.94×10^{-26}	3.62×10^{-27}	5.4

Initial polymer concentration in water is 5 g/L. Oil volume fraction is 10%

[a] Dodecane/Water interfacial tension measured at a polymer concentration of 5 g/L

[b] The precision of the size measurement is ±5 nm

expression of ω. Later, a correcting factor, k, was introduced to account for the dependence of ω on ϕ [41–43]:

$$\omega(\phi) = k(\phi)\ \omega(0) \tag{3}$$

In Eq. (3), $\omega(0)$ corresponds to the value calculated by Eq. (2), and $k(\phi)$ is the correcting factor that depends on oil volume fraction. In previous work, we showed that the available values of $k(\phi)$ overestimate the increase of ω with ϕ [38]. A similar result has been reported previously by Taylor [44]. This fact could be explained by the theoretical derivations of $k(\phi)$ that ignore the presence of the surfactant on the droplets surface.

When comparing the experimental rates of Ostwald ripening to the calculated ones, for dodecane-in-water emulsions, it appears that the experimental rates are six times larger than the calculated ones for the DexP$_\tau$org series and four times for the DexP$_\tau$aq series (Table 6). For the physical data of dodecane, we used the same values as in a previous work [33]: D=5.2×10^{-10} m^2/s, V_m=2.27×10^{-4} m^3/mol and C_∞=2.2×10^{-5} mol/m^3. The rate of Ostwald ripening is approximately proportional to the oil–water interfacial tension measured independently with the same polymer concentration (Fig. 4). Moreover, the experimental points of the DexP$_\tau$aq series are consistent with previously published data of other authors [32]. Finally, we can notice that the two series of modified dextrans, DexP$_\tau$org and DexP$_\tau$aq, give consistent results (Fig. 4).

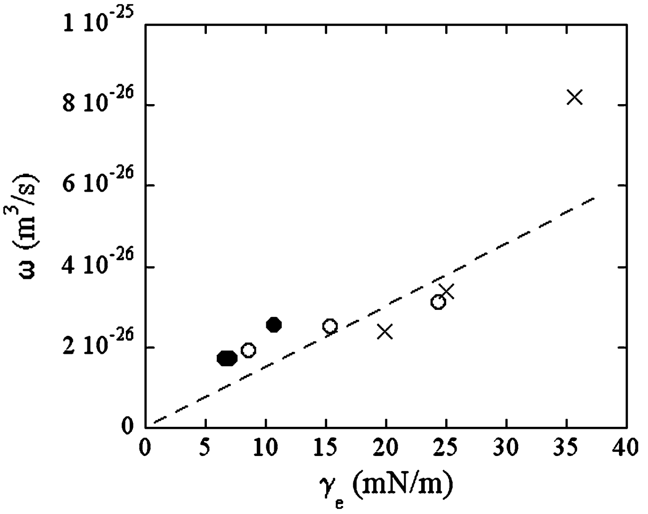


Fig. 4 Rate of Ostwald ripening vs the interfacial tension measured for the same polymer concentration. Dodecane-in-water emulsions (10% oil volume). ● DexP$_\tau$org, ○ DexP$_\tau$aq (this study), × DexP$_\tau$aq [32]. *Dashed line* is curve fitting according to Eq. (2)

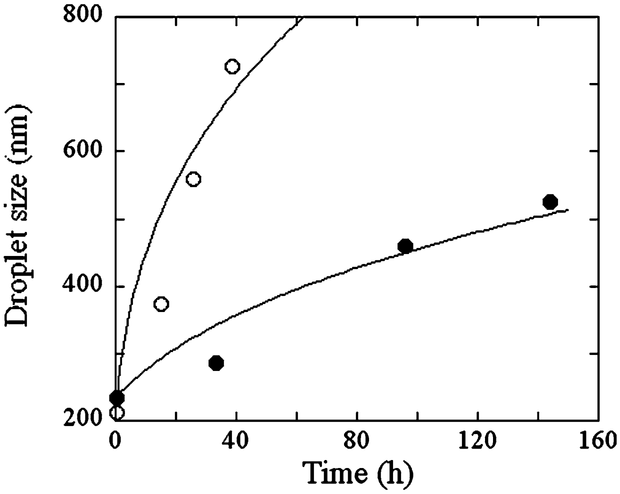


Fig. 5 Variation of droplet size with time for water-in-dichloromethane emulsions with various ionic strengths in the aqueous phase (10% aqueous phase in volume). The concentration of DexP$_{180}$org is 5 g/L in dichloromethane. ● 0.1 M NaCl, ○ 0.1 M Na$_2$CO$_3$. *Line* is curve fitting by Eq. (1)

As for the effect of the degree of substitution on the ageing process, it appears to be similar to that on the surface active behaviour, as predicted by Eq. (2). For the DexP$_\tau$aq series, when τ increases from 6 to 31%, the interfacial tension decreases, and the rate of Ostwald ripening decreases also. Within the DexP$_\tau$org series, when t increases from 17 to 54%, the interfacial tension levels down to around 7 mN/m, so does the rate of Ostwald ripening. This levelling down of the interfacial tension could result from the high density of phenoxy groups along the dextran chain, leading to a preferential intramolecular aggregation and limiting the availability of phenoxy groups for adsorption at the oil–water interface [45]. This would be consistent with the solution behaviour of that polymer (see above).

Submicronic inverse emulsions can be prepared only when the polymer is in the continuous oil phase. This is a direct result of the fact that the steric barrier formed by the polymer is required to stabilize the droplets formed. Moreover, the stability of the inverse emulsions with

Table 7 Ostwald ripening rates of dichloromethane-in-water emulsions stabilized by an organo-soluble dextran derivative (DexP$_{180}$org) with different salt concentrations in water

Salt	[Salt] (mol/L)	Initial droplet size (nm)[a]	ω_{exp} (m^3/s)
NaCl	0.05	180	1.73×10^{-26}
	0.1	234	1.91×10^{-26}
	0.5	219	1.61×10^{-26}
	1.0	273	1.65×10^{-26}
	5.0	523	4.77×10^{-26}
Na$_2$CO$_3$	0.1	212	19.0×10^{-26}

Initial polymer concentration in dichloromethane is 5 g/L. Water volume fraction is 10%

[a] The precision of the size measurement is ±5 nm

polymer in the aqueous disperse phase was very low. As a result, we studied the ageing process of inverse emulsions with the polymer initially dissolved in the oil. For water-in-oil emulsions prepared in the presence of DexP_{180}org, we observe that the increase of droplet size is roughly described by Eq. (1) (Fig. 5). Moreover, with pure water emulsion, ageing was too fast to be monitored experimentally. Consequently, sodium chloride was added into the aqueous phase so as to reduce the rate of emulsion ageing thanks to the low solubility of salt in oil, a known effect for emulsions undergoing Ostwald ripening [46]. These results allow the assumption that the major ageing process is also Ostwald ripening. To ascertain that conclusion, we should also follow how the whole size distribution varies during ageing. This has been already studied for direct emulsions stabilized by modified dextrans [32].

The presence of salt in the aqueous phase leads to Ostwald ripening rates of the same order of magnitude as those of the direct dodecane-in-water emulsions. For sodium chloride concentrations between 0.05 and 1 M, only a slight decrease of the rate of Ostwald ripening is observed (Table 7). Conversely, the initial droplet size tends to increase. For a high NaCl concentration (5 M), the initial droplet size rises up to more than 500 nm, and the ageing rate is multiplied by 3. On the contrary, replacing sodium chloride by sodium carbonate leads to a significant increase of ageing rate (Fig. 5; Table 7). Polymer adsorption at the dichloromethane/water interface seems to be disturbed by a salting-out effect. Because of the presence of numerous aromatic rings along the polysaccharide chains, the adsorption of the polymer at oil–water interface is difficult when the affinity for the aqueous medium is decreased. This may occur at high NaCl concentrations and could explain the variation of both the ageing rate and the initial droplet size. The fact that Na_2CO_3 has a more pronounced effect is consistent with scale of salting-out effect indicated by the well-known series of Hofmeister [47, 48]. The same effect of salting-out could be responsible for a modification of the partition coefficient of water between dichloromethane and aqueous phase. As a result, the amount of water solubilized in the dichloromethane could be reduced, thus diminishing the solvent quality for the modified dextran. This could account for the increase of the initial droplet size. Further work has to be performed for precision of that phenomenon.

Conclusion

Two modification procedures were used for the preparation of amphiphilic polysaccharides from dextran. Since the homogeneous process provides much higher modification yield, it seems preferable to obtain highly modified dextrans.

The emulsifying properties of amphiphilic dextrans are examined as a function of the amount of grafted hydrocarbon groups and by varying the modification procedure. The ability to vary the hydrophobic modification of dextran over a wide range (from 0 to 300% degree of substitution) is the key for the obtention of polymeric surfactants with very different emulsifying properties. As a result, direct and inverse emulsions can be obtained according to the polymer and oil employed. The main ageing process is Ostwald ripening for both types of emulsions. For direct emulsions, modified dextrans obtained by the two procedures exhibit similar properties.

Inverse emulsions are obtained with ageing rates comparable to those of direct ones. Nevertheless, only halogenated hydrocarbon oils can be used for the preparation of inverse emulsions with modified dextrans.

The potentialities of direct emulsions stabilized by amphiphilic dextrans for the preparation of polymeric nanoparticles with defined surface characteristics have already been demonstrated [38, 49]. Inverse emulsions stabilized by dextran derivatives could also find applications in that field. Moreover, dextran derivatives soluble in organic solvents offer interesting possibilities in the field of polymeric nanoparticles. These aspects are currently investigated in our laboratory.

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References

1. Landoll LM (1982) J Polym Sci Polym Chem Ed 20:443
2. Hirrien M, Desbrieres J, Rinaudo M (1996) Carbohydr Polym 31:243
3. Merle L, Charpentier D, Mocanu M, Chapelle S (1999) Eur Polym J 35:1
4. Hill A, Candau F, Selb J (1993) Macromolecules 26:4521
5. Candau F, Selb J (1999) Adv Colloid Interface Sci 79:149
6. Rouzes C, Gref R, Leonard M, De Sousa Delgado A, Dellacherie E (2000) J Biomed Mater Res 50:557
7. Schichman SA, Amey RL (1971) J Phys Chem 75:98
8. Wernicke A, Belniak S, Thévenet S, Descotes G, Bouchu A, Queneau Y (1998) J Chem Soc Perkin Trans 1:1179
9. Gagnaire J, Toraman G, Descotes G, Bouchu A, Queneau Y (1999) Tetrahedron Lett 40:2757
10. Gagnaire J, Cornet A, Bouchu A, Descotes G, Queneau Y (2000) Colloids Surf A 172:125
11. Danel M, Gagnaire J, Queneau Y (2002) J Mol Catal A 184:131

12. Basedow AM, Ebert KH, Feigenbutz W (1980) Makromol Chem 181:1071
13. Catiker E, Guner A (1998) Polym Bull 41:223
14. Guner A (1999) J Appl Polym Sci 72:871
15. Guner A (2004) Eur Polym J 40:1587
16. Nouvel C, Ydens I, Degée P, Dubois P, Dellacherie E, Six JL (2002) Polymer 43:1735
17. Fox TG (1956) Bull Am Phys Soc 1:123
18. Slark AT (1997) Polymer 38:4477
19. Rouzes C, Durand A, Leonard M, Dellacherie E (2002) J Colloid Interface Sci 253:217
20. Nichifor M, Carpov A (1999) Eur Polym J 35:2125
21. Akiyoshi K, Deguchi S, Moriguchi N, Yamaguchi S, Sunamoto J (1993) Macromolecules 26:3062
22. Rotureau E, Chassenieux C, Dellacherie E, Durand A (2005) Macromol Chem Phys 206:2038
23. Rotureau E, Dellacherie E, Durand A (2005) Macromolecules 38:4940
24. Sanchez-Chaves M, Arranz F (1985) Makromol Chem 186:17
25. Ydens I, Rutot D, Degee P, Six JL, Dellacherie E, Dubois P (2000) Macromolecules 33:6713
26. Nouvel C, Frochot C, Sadtler V, Dubois P, Dellacherie E, Six JL (2004) Macromolecules 37:4981
27. Sanchez-Chaves M, Arranz F (1983) Angew Makromol Chem 118:53
28. Reinhart T, Bauer KH (1995) Pharmazie 50:403
29. Bauer KH, Reinhart T, Stenz R (1997) Macromol Symp 120:39
30. Lu M, Albertsson PA, Johansson G, Tjerneld F (1994) J Chromatogr A 668:215
31. Imbert P, Sadtler V, Dellacherie E (2002) Colloids Surf A 211:157
32. Sadtler V, Imbert P, Dellacherie E (2002) J Colloid Interface Sci 254:355
33. Rotureau E, Leonard M, Dellacherie E, Durand A (2004) Phys Chem Chem Phys 6:1430
34. Bancroft WD (1913) J Phys Chem 17:501
35. Schultz PC, Rodriguez MS, Del Blanco LF, Pistonesi M, Agullo E (1998) Colloid Polym Sci 276:1159
36. Perrin P, Monfreux N, Lafuma F (1999) Colloid Polym Sci 277:89
37. Egger H, Scottmann T, Strey R, Valero C, Berkessel A (2002) Tenside Surfactants Deterg 39:17
38. Durand A, Marie E, Rotureau E, Leonard M, Dellacherie E (2004) Langmuir 20:6956
39. Lifshitz IM, Slyozov VV (1961) J Phys Chem Solids 19:35
40. Wagner C (1961) Z Elektrochem 35:581
41. Brailsford AD, Wynblatt P (1979) Acta Metall 27:489
42. Enomoto Y, Tokuyama M, Kawasaki K (1986) Acta Metall 34:2119
43. Taylor P (1998) Adv Colloid Interface Sci 75:107
44. Taylor P (1995) Colloids Surf A 99:175
45. Millet F, Nedyalkov M, Renard B, Perrin P, Lafuma F, Benattar JJ (1999) Langmuir 15:2112
46. Higuchi WI, Misra J (1962) J Pharm Sci 51:459
47. Collins KD, Washabaugh MW (1985) Q Rev Biophys 18:323
48. Collins KD (1997) Biophys J 72:65
49. Rouzes C, Leonard M, Durand A, Dellacherie E (2003) Colloids Surf B 32:125